MERCURY EMISSIONS AT FGD-EQUIPPED COAL-FIRED UTILITIES

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INTRODUCTION AND BACKGROUND

The Environmental Protection Agency (EPA), the U.S. Department of Energy (DOE), the Electric Power Research Institute (EPRI), and their subcontractors have extensively studied the partitioning of Hazardous Air Pollutants (HAPs) at coal-fired utility plants. The majority of HAPs are captured in existing particulate collection devices (ESPs, fabric filters). The exceptions are the elements or compounds denoted as Class III (Hg, Se, HF, HCl), which, because of their volatility, remain in the vapor state at the ESP or fabric filter exit. Potential HAP regulations could impact the U.S. coal and electric utility industry.

Studies at coal-fired utilities have shown that wet scrubbers can remove mercury. However, the studies show a wide variation in removal (0 to 100%), indicating the need for additional data to define the cause of the reported variation. The goal of this program is to develop more precise data regarding the removal of mercury by wet FGD systems. These data, along with EPA and DOE emission assessment results, will provide the U.S. utility industry with information to evaluate the removal achieved by wet FGD systems for volatile HAPs. The data will be used to develop a model to predict HAP removal by wet FGD systems.

This work was funded by CONSOL Inc., the Illinois Clean Coal Institute, the Illinois State Geological Survey, and the U.S. Department of Energy's Federal Energy Technology Center (FETC). The FETC contract coordinator is Tom Brown. The contract, No. DE-AC22-96PC01387, covers the period September 1, 1996, to August 31, 1997.

OBJECTIVES

The goal of the project is to determine the mercury (Hg) removal achieved by wet FGD processes at coal-fired utility plants, and to correlate Hg removal with coal properties and boiler/scrubber operating parameters. The sampling program was conducted by the CONSOL Research & Development field services staff. CONSOL R&D, with assistance from the Illinois State Geological Survey (ISGS), is correlating the Hg removal with boiler/scrubber operating parameters. Most mercury, because of its volatility, is not captured with the fly ash and remains in the vapor state at the exit of the particulate collection devices (ESPs, fabric filters). The potential Hg regulations are a concern to the coal and utility industries. The data from this study will help to determine the effectiveness of wet FGD systems to remove Hg. Three utility plants were evaluated; two additional plants may be evaluated during 1997-1998.

EXPERIMENTAL PROCEDURES

Hg SAMPLING METHODS

Three utility stations equipped with wet scrubbers agreed to participate with CONSOL in the test program. Site visits were conducted at all stations by the CONSOL sampling team. During the site visits, program requirements were discussed with plant operating personnel, sampling locations were identified, and arrangements were made with plant personnel to provide assistance during the sampling program.

Four material balance tests were conducted at the first and second station and three at the third station. Each test period included simultaneous flue gas sampling at the ESP inlet and at the stack. These samples were obtained using a modified EPA Method 29 sampling train and/or the Ontario Hydro Hg speciation method. The EPA Method 29 train was modified by incorporating two deionized water (DI) water impingers prior to the nitric acid/peroxide impingers.[1] The two DI impingers simultaneously collected the acid gases (HCl and HF), and speciated the gas phase Hg emissions. The Ontario Hydro Hg method uses three KCl-filled impingers to collect the oxidized Hg species. The KCl impingers are followed by H_2O_2 impingers to remove SO_2, which are followed by acidified $KMnO_4$ impingers to collect elemental Hg. In addition to flue gas samples, representative process stream samples were obtained periodically during the test period (from the boiler and scrubber). Process stream samples included: coal, coal-mill rejects, ash (bottom, economizer, ESP), limestone slurry, scrubber make-up water, scrubber by-product (gypsum, sludge), and scrubber discharge water. The chemical analyses of these samples and the mass flow rate of these streams, are used to calculate material balances.

During the test periods, pertinent boiler and scrubber operating data were periodically obtained to ensure steady-state plant operation. Complete logs of boiler and scrubber operating data were supplied to CONSOL by the stations.

Process stream samples collected from the stations were analyzed for Hg to determine the Hg removal across the scrubbers. These samples also were analyzed for major ash elements (Fe, Si, Al, etc.) to evaluate the material balances. Standard analytical procedures were used to analyze the flue gas and process stream samples.

UTILITY OPERATING CONDITIONS

One objective of the test program was to determine the accuracy and reliability of existing mercury-in-flue-gas measurement techniques. This required repetitive measurements taken under similar conditions. The operating staff at each utility was asked to maintain similar boiler and scrubber operating conditions for each test period. The first test site is a 280 MWe pulverized coal-fired boiler. The second test site is a 200 MWe pulverized coal-fired boiler. The third test site is a 180 MWe coal-fired cyclone boiler. The following table shows the operating parameters maintained at each facility during the sampling programs.

BOILER/SCRUBBER OPERATING PARAMETERS

	Plant 1, 280 MWe	Plant 2, 200 MWe	Plant 3, 180 MWe
Boiler Configuration	Pulverized Coal	Pulverized Coal	Cyclone
Megawatts	290	193	180
Coal Feed, tph	100	88	90
% O_2 @ Economizer	3.0	3.5	2.3
Flue Gas Parameters			
Flow, kscfh	52500	38800	29400
% CO_2	12.6	11.1	13.3
% O_2	6.5	7.5	4.9
SO_2 lb/MM Btu	0.18	1.05	0.74
SO_2 lb/hr	460	2035	1335
% Opacity	<5	6.6	5.8
Scrubber Parameters			
Limestone Use, tph	ND	17.4	11.0
Limestone Slurry % Solids	31.6	ND	32.5
FGD Slurry Density, g/cc	ND	1.08	ND
FGD Slurry pH	6.5	6.1	5.8
L/G Ratio	60-75	94	73
SO_2 Removal, %	97	82	87

Plant 1 is equipped with a thiosorbic-lime scrubber, Plant 2 is equipped with a conventional forced-oxidation limestone scrubber, and Plant 3 is equipped with a conventional limestone scrubber. The SO_2 removal efficiency ranged from 82% to 97%.

COAL ANALYSES

The literature suggests that coal composition can influence Hg speciation in the flue gas. Comprehensive coal analyses were conducted on daily test coal samples from each plant. Little variability was observed in these daily samples. The average coal analyses results from samples collected at the three test sites are given in the following table. All of the plants were firing bituminous coal. Plant 1 fired an Appalachian Basin, high-volatile bituminous coal. Plants 2 and 3 fired Illinois Basin bituminous coals. While some of the coal quality parameters had significant differences (ash, Btu), the coals had similar sulfur, Hg, and chlorine concentrations. There were no major differences observed in the Hg speciation results for these coals.

ANALYSIS OF COAL FEED SAMPLES

(Units are % dry basis unless noted)

	Plant 1	Plant 2	Plant 3
Volatile Matter	36.72	41.24	32.49
Ash	13.89	10.93	18.51
Carbon	73.60	70.60	66.31
Hydrogen	4.81	5.05	4.13
Nitrogen	1.41	1.45	1.47
Oxygen	2.84	8.20	6.05
Total Sulfur	3.52	3.78	3.54
Pyritic Sulfur	2.01	2.06	2.13
Sulfate Sulfur	0.03	0.05	0.22
Organic Sulfur	1.48	1.67	1.19
Chlorine	0.11	0.16	0.11
Mercury, ppm	0.124	0.086	0.092
Heating Value, Btu/lb	13130	12737	11729

RESULTS AND DISCUSSION

MERCURY REMOVAL DUE TO ADSORPTION ON FLY ASH

The Hg removal due to adsorption on the fly ash was determined by calculating the Hg input to the boiler from the coal Hg concentration and the coal firing rate. The only ash stream that contained absorbed Hg was the ESP ash. The mass flow rate of Hg on the ESP ash was determined from the analysis of the ESP hopper ash samples and ESP flue gas particulate mass flow rate. The calculated Hg removal due to adsorption on the fly ash at each plant is shown in the following table.

Hg REMOVAL DUE ADSORPTION ON FLY ASH

% of Total Hg Input

	Plant 1	Plant 2	Plant 3
Test 1	23	5	14
Test 2	15	8	11
Test 3	39	8	15
Test 4	17	6	---
Average	**24**	**7**	**13**
Standard Deviation	11	2	2
PRSD*	46%	22%	16%

*Percent relative standard deviation

The first plant had an average mercury reduction of 24%; the second plant had a 7% reduction; and the third plant had a 13% reduction. The data indicate that a significant fraction of mercury is collected on the ESP ash. The unburned carbon concentrations in the ESP ashes ranged from 3 to 5% for Plant 1, 0.8 to 1.2% for Plant 2, and 32 to 38% for Plant 3. For Plant 1, the Hg removals showed a significant correlation with unburned carbon concentration. There was no similar correlation for the Plant 2 or Plant 3 results.

MERCURY REMOVAL ACROSS THE FGD SYSTEM

The Hg removal across the FGD system was determined by two methods. In the first method, the flue gas Hg concentration at the FGD inlet was calculated from the coal firing rate and Hg content, and Hg absorbed on fly ash. In the second method, actual gas phase Hg measurements at the FGD inlet were used. The inlet Hg concentrations were compared to the stack flue gas Hg measurements to quantify Hg removal. The results are shown in the following table.

Hg REMOVAL ACROSS FGD SYSTEM - % of Total Hg Input

	Plant 1		Plant 2		Plant 3	
	Coal Value	**Gas Samples**	**Coal Value**	**Gas Samples**	**Coal Value**	**Gas Samples**
Test 1	59	63	63	---	58	68
Test 2	58	59	51	65	69	77
Test 3	44	48	48	53	46	57
Test 4	67	54	48	50	---	---
Average	**57**	**56**	**52**	**56**	**58**	**67**
Std. Dev.	10	6	7	8	11	10
PRSD	18%	11%	14%	14%	20%	15%

The first test site had a 57% average Hg removal across the FGD using the coal data and a 56% removal using the gas sampling data. The good agreement between the two techniques confirms the measured Hg removal. The second site had a 52% Hg removal using the coal data and a 56% removal using the gas sampling data. Again, this is fairly good agreement. The third plant had a 58% average removal using the coal data and 67% using the gas sampling data. The accuracy of the Hg inlet value calculated from the coal data is a function of the quality of the mercury-in-coal analysis, the calculated firing rate, and the measured ESP Hg removal. The accuracy of the Hg inlet value from the gas analysis is strictly a function of the accuracy the impinger analysis for Hg. These data indicate that Hg removal across the FGD system is ~55% for Plants 1 and 2 and 58% to 67% for Plant 3.

TOTAL Hg REMOVAL ACROSS UTILITY SYSTEM

This test program confirmed that there is Hg removal by adsorption on the ESP fly ash particles and gas phase Hg removal across the FGD system. The combined Hg removal across the ESP and FGD is the total Hg removal across the system. The total Hg removal is the difference between the Hg input, calculated using the coal firing rate and coal Hg concentration, and the Hg emissions, as measured in the stack flue gas sample. Total Hg removal for all three plants are shown in the following table.

TOTAL Hg REMOVAL ACROSS ESP and FGD - % of Total Hg Input

	Plant 1	Plant 2	Plant 3
Test 1	71	68	73
Test 2	65	60	80
Test 3	67	56	62
Test 4	64	53	---
Average	**67**	**59**	**72**
Standard Deviation	3	6	9
PRSD	5%	11%	13%

Total Hg removal averaged 67% for the first plant, 59% for the second plant, and 72% for the third plant. There was a measured relative variability of ±5% to 13%. The data indicate that about two-thirds of the Hg in the coal is removed. These measurements were obtained during normal and routine operations, and no adjustments were made to optimize Hg removal.

FATE OF Hg IN UTILITY SYSTEM AND MATERIAL BALANCE DATA

In addition to the measurement of Hg removal in FGD-equipped utility systems, two additional objectives were to determine the fate of the removed Hg and to calculate Hg material balance closures to assess the quality of the measurements. Representative process stream samples that augmented the flue gas measurements were obtained and analyzed to complete this task. The results of these measurements for each plant are shown below.

FATE OF Hg AND MATERIAL BALANCE DATA
(Hg mass flow, mg/sec)

	Plant 1	Plant 2	Plant 3
Input Streams:			
Coal	3.09	1.65	1.76
Limestone	0	0	0
Make-up Water	0	0	0
Total Hg Input	**3.09**	**1.65**	**1.76**
Output Streams:			
Mill Reject	0	0	NA
Bottom Ash	0	0	0
Economizer Ash	0	0	0
ESP Ash	0.74 (24%)	0.11 (7%)	0.24 (14%)
FGD Solids	1.38 (45%)	0.67 (41%)	1.27 (72%)
FGD Filtrate	0	0	0
Stack Emissions	1.06 (34%)	0.67 (41%)	0.49 (28%)
Total Outlet	**3.17**	**1.39**	**1.79**
% Hg Closure	**103%**	**85%**	**115%**

All of the plants had similar results. The only significant mercury input was due to the coal. A very small amount of the mercury was removed with the coal mill rejects, but the level was

insignificant for the balance. No Hg is removed in the ash prior to the air preheater (bottom and economizer ash samples). The only output streams containing Hg are the ESP solids, the FGD solids, and the stack emissions. The majority of the Hg removed across the scrubber can be accounted for by the Hg in the FGD solids. No mercury was detected in the FGD filtrate water. The Hg balance closures for the first plant ranged from 90% to 131% and averaged 103%. The Hg balance closures for the second plant ranged from 72% to 92% and averaged 85%. The Hg balance closures for the third plant ranged from 107% to 123% and averaged 115%. For the three plants, eleven Hg material balance studies were completed in total. The Hg material balance closures were between 72% and 131%. The grand average for the eleven tests was 100%. For this type of testing, the data quality objective was an average material balance closure of ±20%, with no test greater than ±30%. These objectives were met.

MERCURY SPECIATION AND REMOVAL ACROSS THE ESP AND FGD

Hg speciation results can give valuable insight into the removal mechanism. Total Hg and Hg speciation at the ESP inlet and at the stack are presented in Figures 1-3. In these figures, the concentration of the Hg species measured is shown in a stacked bar graph. The arrow designates the Hg material balance at the ESP inlet.

Plant 1 - The speciation data for each test completed at Plant 1 are shown in Figure 1. The Hg material balance closure at the ESP inlet was excellent. The equivalent gas phase Hg concentration reporting to the ESP ash varied from 1.5 to 4 $\mu g/m^3$. This fraction of Hg was removed from the flue gas by the ESP. The Hg emissions were consistent, ranging from 3.0 to 3.8 $\mu g/m^3$. In this program, the gas phase values were obtained using the Method 29 sampling train. In Method 29, it is assumed that the Hg collected in the nitric acid/peroxide impingers is oxidized and the Hg collected in the permanganate impingers is elemental. A comparison of the inlet and outlet estimate of the oxidized Hg fraction shows almost total removal for this species. No Hg was found on the particulate filter at the FGD outlet. A similar comparison of the estimated elemental Hg fraction shows a slight increase across the FGD.

Plant 2 - The material balance closure at the ESP inlet for the first test at Plant 2 was high, but excellent closures were obtained for the following three tests, as shown in Figure 2. At the ESP inlet, the estimated oxidized mercury fraction was the dominant species. At Plant 2, the inlet gas phase Hg concentrations were obtained from the Ontario Hydro train. In this train, it is assumed that the Hg collected in the first three KCl impingers is oxidized and the Hg collected in the permanganate impingers is elemental. The scrubber outlet mercury samples were obtained using a modified Method 29 train with DI water in the first two impingers, nitric acid/peroxide in the next two impingers, and permanganate in the final two impingers. The Hg collected in the impingers upstream of the permanganate is assumed to be oxidized, while the Hg collected in the permanganate impingers is assumed to be elemental. The total Hg emissions at the outlet showed excellent reproducibility, ranging from 1.9 to 2.8 $\mu g/m^3$. The majority of the Hg emissions are elemental mercury. However, some Hg was observed on the particulate filter. These data suggest that the mercury species collected in the KCl impingers, or the oxidized estimate, is the species removed across the scrubber. A slight increase in elemental mercury across the scrubber was again observed.

Plant 3 - Three tests were conducted with excellent mercury closures at the ESP inlet (Figure 3). As in the previous cases, the estimated oxidized mercury fraction is the dominate species at the ESP outlet. The total ESP inlet Hg concentration ranged between 11.6 and 12.2 $\mu g/m^3$. The outlet measurements indicate significant particulate and elemental Hg fractions and a very small oxidized Hg concentration. The outlet Hg concentrations were between 2.5 and 4.8 $\mu g/m^3$. The particulate fraction at the scrubber outlet is probably FGD solids carryover that contains captured mercury and may be a function of the efficiency of the mist eliminator.

If it is assumed that the Hg adsorbed on the fly ash and the Hg collected in the KCl impingers is oxidized Hg, the ratio of oxidized to elemental Hg at the three plants is ~8:1. Very low concentrations of oxidized Hg (estimated from the sampling train impinger solutions) were measured in the stack flue gas . The majority of the estimated oxidized mercury is removed by the ESP/FGD combination. There was no decrease, and in some cases there was an increase, in the estimated elemental Hg concentration across the FGD. These data clearly show that the Hg species collected in the nitric acid/peroxide impingers of the Method 29 train and the KCl impingers of the Ontario Hydro sampling train is the species that is being removed across the FGD system.

The cause of the observed increase in the estimate of the elemental Hg fraction at the FGD outlet is unknown and requires additional investigation. This increase could be due to artifact formation in the sampling trains or due to the reduction of some fraction of the oxidized to elemental Hg in the FGD system.

STATISTICAL ANALYSIS OF PARAMETERS INFLUENCING HG REMOVAL

A review of the existing data indicates no correlation of coal quality, boiler operations, or scrubber parameters with Hg removal. However, these data are very limited. Additional statistical analyses were completed on the data from this study combined with data available in the literature. Again, no clear correlations were identified. There was no correlation between SO_2 removal or the scrubber L/G ratio with the observed Hg removal. The statistical analysis is inconclusive due to the similarities in the coals and facilities tested. A greater range in coal quality variables is needed.

APPLICATION

The U.S. EPA has prepared a report to Congress regarding U.S. mercury emissions and heath effects. Coal-fired electric utilities have been identified as the third largest contributing Hg source. Initial cost estimates for the removal of Hg from coal-fired utilities range from $10 million to $40 million per ton of Hg removed. For comparison purposes, the cost effectiveness of SO_2 and NOx removal is between $70 and $300 per ton of SO_2 removed and between $150 and $3,000 per ton of NOx removed. Clearly, Hg control costs are very high. Controlling Hg emissions with existing FGD systems would not increase FGD or plant costs; the cost effectiveness of FGD Hg control is $0 per ton of Hg removed. Information documenting the level of Hg control achieved by ESP/FGD systems and identifying the process parameters that influence Hg removal will provide utilities and regulators control options if Hg regulations are imposed.

CONCLUSIONS

A mercury measurement program was conducted at three full-scale, coal-fired utilities equipped with lime and limestone FGD scrubbers.

A preliminary statistical analysis of the available Hg emission data from scrubbed utilities showed no significant correlation of removal with process variables.

A mercury sampling program was completed at three FGD-equipped utility boilers during normal and routine plant and scrubber operations. The mercury emissions averaged 3.4 $\mu g/m^3$ (0.008 lb/hr) for the first plant, 2.9 $\mu g/m^3$ (0.005 lb/hr) for the second plant, and 3.5 $\mu g/m^3$ (0.004 lb/hr) for the third plant.

The mercury removal due to adsorption on the ESP fly ash was between 7% and 24%. In one of three cases, this removal correlated with the carbon content of the ESP ash.

The mercury removal across the FGD averaged ~55% for the first and second plants and 58-67% for the third plant. The total system (ESP and FGD) removal averaged 67 ±3% for the first plant, 59 ±6% for the second plant, and 72 ±9% for the third plant.

The Hg material balance closures were between 72% and 131% for the 11 test periods. The grand average closure was 100%. The material balances are within data quality objectives.

The ESP inlet and stack flue gas speciation data indicate that the oxidized Hg fraction is removed across the FGD scrubber. The outlet speciation data showed very little oxidized Hg. However, significant levels of particulate and elemental Hg were observed.

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REFERENCES

1. ASTM Committee D-22.03.03 Draft Document.

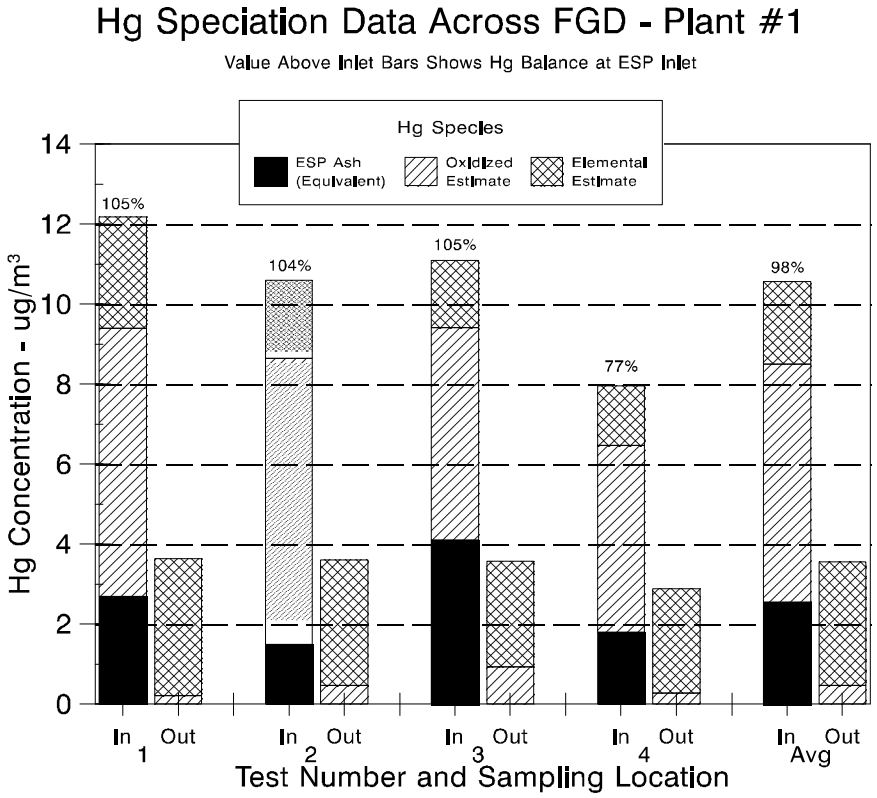

Figure 1 - ESP Inlet and FGD Outlet Flue Gas Hg Speciation Results for Plant 1.

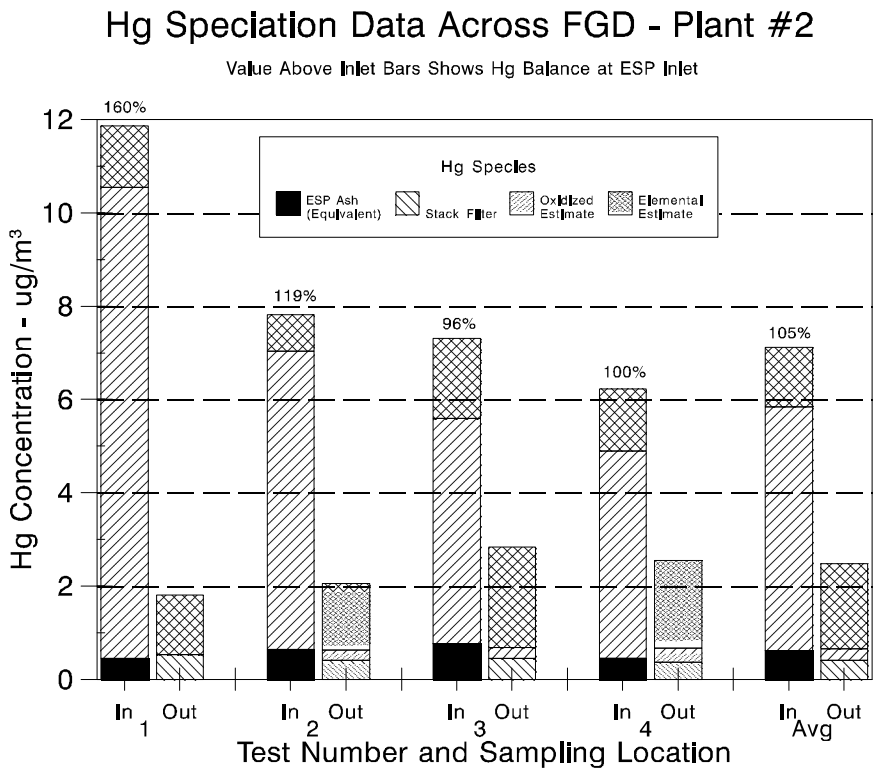

Figure 2 - ESP Inlet and FGD Outlet Flue Gas Hg Speciation Results for Plant 2.

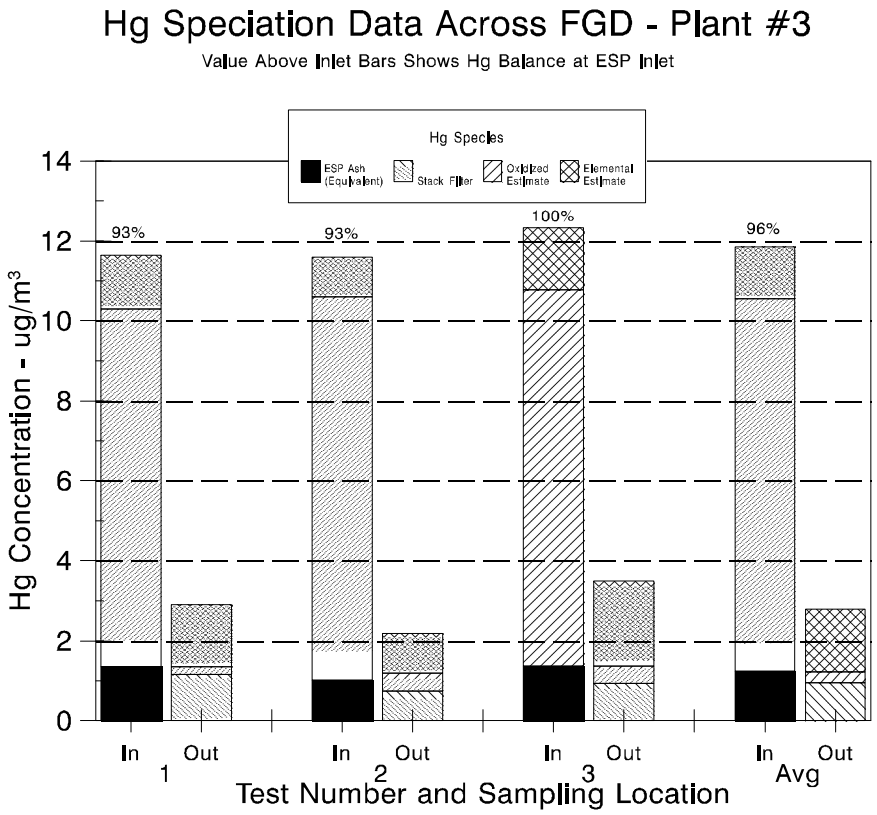

Figure 3 - ESP Inlet and FGD Outlet Flue Gas Hg Speciation Results for Plant 3.